Growth of AlN oriented films on insulating substrates

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***Abstract*— This work describes the structural and piezoelectric assessment of aluminum nitride (AlN) thin films deposited by pulsed-DC reactive sputtering on insulating substrates. We investigate the effect of different insulating seed layers on AlN properties (crystallinity, residual stress and piezoelectric activity). The seed layers investigated, silicon nitride (Si_3N_4), silicon dioxide (SiO_2), amorphous tantalum oxide (Ta_2O_5), and amorphous or nano-crystalline titanium oxide (TiO_2) are deposited on glass plates to a thickness lower than 100 nm. Before AlN films deposition, their surface is pre-treated with a soft ionic cleaning, either with argon or nitrogen ions. Only AlN films grown of TiO_2 seed layers exhibit a significant piezoelectric activity to be used in acoustic device applications. Pure c-axis oriented films, with FWHM of rocking curve of 6º, stress below 500 MPa, and electromechanical coupling factors measured in SAW devices of 1.25% are obtained. The best AlN films are achieved on amorphous TiO_2 seed layers deposited at high target power and low sputtering pressure. On the other hand, AlN films deposited on Si_3N_4, SiO_2 and TaO_x exhibit a mixed orientation, high stress and very low piezoelectric activity, which invalidate their use in acoustic devices.**

I. INTRODUCTION

The growth of AlN thin films with good crystal quality and piezoelectric activity on insulating thin films is still a pending matter, as the oriented growth of AlN requires specific surface conditions, which are mainly achieved in metallic layers (Ir, Ru, Pt, W or Mo) [1], or single crystal insulating substrates, such as sapphire, quartz or lithium niobate [2]. However, these layered structures are required in many applications, such as surface acoustic wave (SAW) devices [2], laterally excited shear mode resonators [3] or bulk acoustic wave (BAW) composite resonators with insulating layers for temperature compensation [4]. AlN films are frequently grown over silicon dioxide (SiO_2) thin films; actually, AlN films with significant piezoelectric activity deposited on SiO_2 substrates have been reported recently [5]. To achieve highly c-axis oriented AlN films in SiO_2 substrates, the deposition process has to be tuned carefully, which generally requires a considerable increase of the voltage bias applied to the substrates. This causes a severe increase of the compressive residual stress of the AlN films, as we reported in our previous investigations on RF-sputtered AlN films on SiO_2 [6]. Moreover, AlN deposition is critically dependent on the deposition system, as the energetic bombardment of the film during growth depends on the chamber geometry and on the electric and magnetic fields arrangement [7]. In order to reduce the stress built on the films undergoing a severe energetic bombardment, we have investigated the effect of using a thin insulating interlayer that would act as a seed layer for the growth of c-axis oriented AlN films. This would allow to reduce the energy feed to the substrate required to achieve well oriented films. We have investigated the growth of AlN on silicon nitride (Si_3N_4), tantalum oxide (Ta_2O_5), sputtered SiO_2 and TiO_2. The sputtering process of Si_3N_4, Ta_2O_5 and SiO_2 had been already studied in previous works by the authors [8-9]. Since the best preliminary results were achieved when using TiO_2 seed layers, the present work is mainly focused on the study of the TiO_2 deposition process in order to set the optimum conditions for the growth of high quality AlN films.

TiO_2 thin films are widely used in different field, such as optical-interference coatings [10], coatings for catalyst applications [11], and coatings for the biocompatibility of bone implants [12]. Titanium dioxide exists in both amorphous and crystalline form; this last comprises two crystalline polymorph phases, anatase and rutile, of tetragonal structure. The rutile phase more stable thermodynamically [13] but the more hard to obtain. There are many methods for the preparation of TiO_2 films, such as chemical vapor deposition, ion beam-assisted deposition, reactive evaporation, sol-gel processes, and sputtering [14-18]. In particular, a magnetron sputtering technique seems to be the most favorable method. Most of the TiO_2 films prepared by the above-mentioned methods are either amorphous or nano-crystalline (anatase) and have to be heated to high temperatures (around 600 °C and above) to achieve the rutile crystalline phase [19]. According to [19], TiO_2 films deposited without substrate heating by dc-sputtering exhibit the anatase phase.

In summary, we explore the possibility of growing *c*-axis oriented AlN thin films by pulsed-dc sputtering on insulating glass substrates covered by different seed layers (specially TiO_2), paying a special attention to the influence of their crystalline properties and to the preconditioning of their surface by in-situ ion bombardment just before AlN deposition.

II. EXPERIMENTAL

A. Sputtering Process

The seed layers investigated (Si_3N_4, Ta_2O_5, SiO_2, and TiO_2) were deposited in a Leybold Z- 550 system by a pulsed-DC reactive magnetron sputtering process. High-purity Si, Ta and Ti targets 150 mm-in-diameter were sputtered using Ar/O_2 mixtures of different composition. The deposition process of both SiO_2 and TaO_x films had been extensively studied previously; details of the film characteristics as a function of the sputter parameters can be found in earlier works [8, 9]. The sputtering process of the TiO_2 films was carried out by applying to the Ti target a pulsed-DC power of 50 kHz and duty cycle of 75% ranging from 200 W to 800 W. The total pressure in the chamber was varied between 1.5 mTorr and 3.3 mTorr and the percentage of O_2 in the gas between 30% and 100%. During the deposition process the substrates were not intentionally heated. In all cases, the thickness of the seed layer varied between 50 nm and 100 nm.

The sputter process of the Ti target in Ar/O_2 atmospheres exhibited a transitory behavior, similar to that of any metallic target undergoing a reactive sputtering process at constant power under oxygen atmospheres, owing the oxidation of its surface. We experimentally checked that any TiO_2 film deposited in the metallic regime exhibited a conductive behavior, regardless of the deposition conditions. Hence, all the samples investigated here were grown in the poisoned regime. For each pulsed DC power we determined first the minimum gas pressure necessary to switch on the discharge in the chamber. Then the gas ratio was adjusted until the target switched to the poisoned regime, which was controlled by monitoring the evolution of its voltage. Once the voltage stabilized, a first layer was deposited under these conditions (close to the metallic/poisoned transition). Then, the oxygen ratio was the increased considerably while keeping constant the total pressure, in order to grow a second layer in the deep poisoned regime (far from the transition).

The films were deposited on Corning glass plates 500 μm-thick and on (100) silicon wafers for IR transmission and reflection measurements. Before AlN deposition the substrates were degassed close to the AlN deposition temperature (400 ºC). Then, the surface of the seed layers were soft etched by means of a short bombardment (60 s) with Ar^+ or N_2^+ ions from an RF glow discharge generated near the substrate. Once the surface prepared, the AlN films were sputtered on top of the seed layers using a 3:7 $Ar:N_2$ admixture at a total pressure of 1.2 mTorr, a pulsed-DC power of 1.2 kW and a platen temperature of 400ºC. An RF bias of -77 V was applied to the substrates to tune the stress in the AlN films. These conditions provided deposition rates of 40 $nm \cdot min^{-1}$. The thickness of the AlN film always was around 1 μm. We have experimentally checked that these deposition conditions provide AlN films of excellent crystal quality and piezoelectric response when deposited on metallic electrodes (Ir or Mo) [20].

In order to asses the piezoelectric activity of the AlN films, SAW delay lines were fabricated in the surface of the AlN films by defining interdigital transducers (IDTs) on a Mo film 100 nm-thick. Each IDT had 40 pairs of bars separated 10 μm, corresponding thus to a wavelength of 40 μm. SAW delay lines were stuck to a test fixture and the pads of the IDTs ultrasonically bonded using 25 μm-wide aluminum wires of 5 to 10 mm. The scattering parameters S_{ij} of the SAW delay lines were measured between 100 kHz and 700 MHz with an Agilent network analyzer PNA N5230A. The experimental spectra were fitted using our own simulation program based on Campbell's method [21], which has been described in a previous work [22]. This model eliminate the effects of the impedance mismatch at the input and output ports due to the non-optimized geometry and to parasitic effects such as the series resistance, the wire inductance, the electromagnetic feedtrough between the IDTs and the effects of the inductance and the resistance in the ground loop. All these non desired effects distort the frequency response of a real delay line. After the fitting, we obtained the electromechanical coupling factor associated to the excitation of a Rayleigh wave in an ideal semi infinite AlN substrate, which we will call k^2_{SAW}; this factor is only dependent on the AlN material properties and independent of the geometry of the layered structure. This k^2_{SAW} is used to compare the piezoelectric performance of the AlN film of the device. Fig. 1 shows the response of three SAW delay lines of AlN films deposited on TiO_2, SiO_2 and Ta_2O_5 seed layers., after de-embedding the parasitic effects.

X-ray diffraction patterns of the processed samples were measured in conventional Bragg-Brentano geometry in a Supratech XPert MRD diffractometer between 2θ = 10º and 2θ = 80º. The in-plane residual stress of the AlN films was derived from the measurement of the curvature of the surface before and after the film deposition using the Stoney's formula.

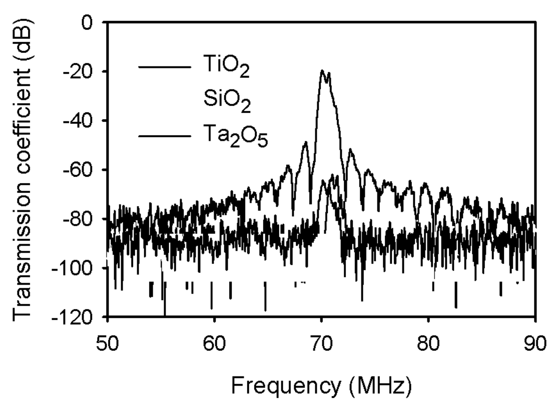

Figure 1. Transmissin coefficient of three SAW delay lines fabricated on AlN deposited on TiO_2, SiO_2 and Ta_2O_5 seed layers.

III. RESULTS AND DISCUSSION

AlN films did not adhere to Si_3N_4 seed layers so these were discarded from the study. On the other hand, AlN films grown on SiO_2 and Ta_2O_5 substrates under standard conditions exhibited a very poor crystallinity with mixed orientations (00·2, 10·3 and 10·2 peaks) and did not possess a significant piezoelectric response as shown in Fig. 1. This type of AlN films have been widely described in [23]. To achieve AlN films on SiO_2 and Ta_2O_5 substrates with a significant piezoelectric activity a great negative polarization has to be applied to the substrate during deposition. This provides 00·2 oriented films with a homogenous polar orientation, as previously discussed in [6]. However, the high substrate bias induces a strong ionic bombardment on the surface of the AlN film during the deposition. As a consequence, the crystal quality dramatically drops and the residual stress increases to values higher than 2 GPa. This high stress induces the films of the layered structure to lift off from the glass substrate. Therefore, SiO_2 and Ta_2O_5 along with Si_3N_4 are not good candidates as seed layers for sputtered AlN films.

AlN films deposited on TiO_2 in similar conditions than those grown on metallic substrates show a definite 00·2 orientation (although with wider rocking curves); additionally, the films possess low residual stress (300 MPa) and a piezoelectric activity good enough to justify their use in acoustic applications. We have found some trends in the variations of the AlN properties with the deposition conditions of the TiO_2 seed layer. The most influent deposition conditions are the power applied to the target, the total pressure and the ionic pretreatment of the TiO_2 seed layer, as will be shown in the following, were we compare the properties of AlN films grown on identical deposition conditions on differently deposited TiO_2 seed layers. Fig. 2 shows the XRD patterns of some AlN films deposited on TiO_2 substrates of different structure.

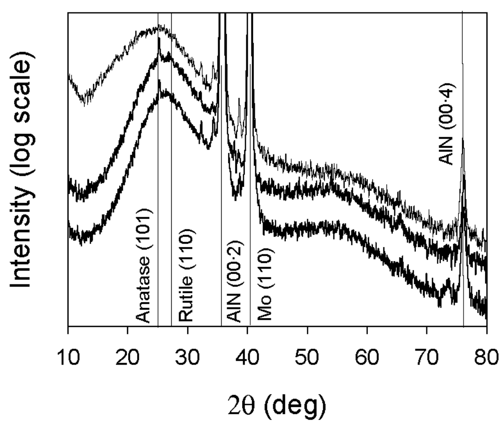

Figure 2. XRD patterns of AlN/ TiO_2 films with different structures.

The most intense peaks correspond to the reflection in the 00·2-AlN and 111-Mo planes, these last coming for the metallic IDTs. In some samples other small peaks that appear in the XRD spectra can be associated to the anatase (2θ = 25.6° and 38.2°) and the rutile (2θ = 27.5°) phases of TiO2. Their very low intensity suggests that the TiO2 films are essentially amorphous although some of them contain small amounts of embedded nano-crystals.

Linking the piezoelectric response of the AlN films with the crystalline characteristics of the TiO_2 seed layers is very difficult. Besides, relating the piezoelectric activity of the AlN films (k^2_{SAW}) with their crystalline characteristics brings surprising results, as the films with a larger piezoelectric activity (k^2_{SAW} ~ 1.25%) exhibit very wide RCs (as high as 16°), whereas films of considerably narrower RCs (~ 6 °) have bad piezoelectric responses, as Fig.3 shows.

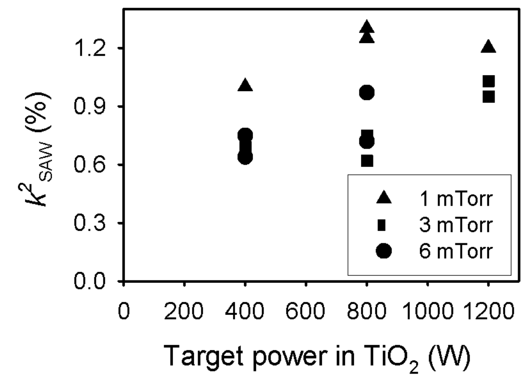

Figure 3. Values of k^2_{SAW} derived from test structures made on several AlN films deposited on TiO_2 seed layers as a function of the FWHM of the RC of the (00·2) AlN direction.

If one keeps in mind that all the AlN films were deposited in the same run under identical condition, the observed behavior only has one explanation: the TiO_2 surface conditions that stimulates the growth of highly oriented AlN and favors the narrowing of RCs is also responsible of the growth of AlN microcrystals with different polar orientations (inversion domains), that partially cancel the piezoelectric response of the films. Therefore, we have tried to find trends between the deposition conditions of TiO_2 films and the piezoelectric activity of the subsequently grown AlN films, assessed through k^2_{SAW}. Fig.4 shows the k^2_{SAW} of the devices as a function of the power applied to the Ti target during TiO_2 deposition.

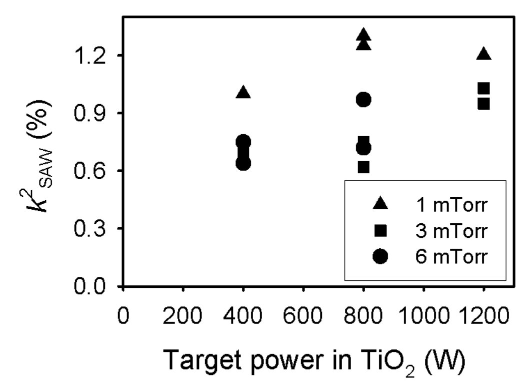

Figure 4. Values of k^2_{SAW} as a function of the target power during TiO_2 seed layer deposition.

According to the data of Fig.4, the piezoelectric activity of the AlN films apparently increase as the DC-pulsed power increases and when the pressure lowers. This indicates that a greater bombardment of the TiO_2 film during its growth can help the growth of AlN films free of inversion domains. At high powers the plasma is denser, so there is a greater amount of ions and electrons in the discharge; furthermore, at low pressures the species impinge on the substrate with supplementary energy because they suffer less collisions with the gas of the discharge. Hence, under these conditions the energy delivered to the substrate is greater, which yields to TiO_2 films with a homogeneous surface state that promotes the growth AlN films with uniform polar orientation. On the other hand, the ionic bombardment undergone by the TiO_2

layers during growth may cause some disorder in the atomic arrangement of the TiO_2 surface, which would be responsible of the widening of the RCs of the AlN films. This same mechanisms causes apparently a reduction of the residual stress, as can be seen in Fig. 5

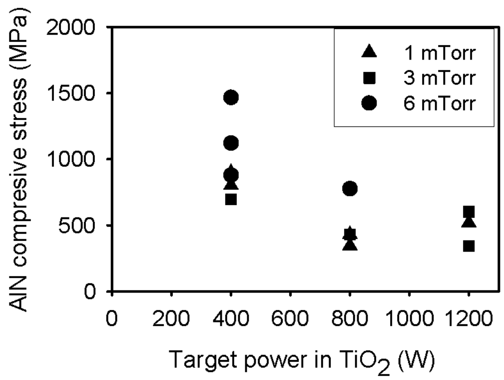

Figure 5. Values of residual stress as a function of the target power during TiO_2 seed layer deposition.

IV. Conclusions

AlN films 1 μm-thick were deposited on glass substrates covered by insulating seed layers of Si_3N_4, SiO_2, Ta_2O_5 and TiO_2. The characteristics of the AlN films (stress, crystal structure and piezoelectric behavior) depended on the nature and structure of the seed layer. AlN films grown on Si_3N_4 had low adherence and tended to peel off. Similarly, AlN deposited on SiO_2 and Ta_2O_5 exhibited a residual stress that was not suitable for device fabrication. TiO_2 seed layers promoted the growth of AlN films with residual stress below 500 MPa, purely (00·2)-oriented, and k^2_{SAW} of up to 1.25%. The piezoelectric activity is not related to the width of the RC around the 00·2 peak. This behavior suggests that the mechanism stimulating the growth of purely oriented (00·2) films with narrow rocking-curve is also responsible of the growth of microcrystals with different polar orientations, which partially cancels the piezoelectric response of the films.

Acknowledgment

This work has been supported by the Ministerio de Ciencia e Innovación of Spain through project MAT2010-18933, and by the Comunidad de Madrid and the UPM through the IV PRICIT programme.

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